REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
05-06-2010	Final Report	15-Sep-2008 - 14-Jun-2009

4. TITLE AND SUBTITLE
Final Progress Report for New Microstructures for Old Monomers: Syntheses of Gradient pi-Conjugated Copolymers.

5a. CONTRACT NUMBER
W911NF-08-1-0450

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
55095-CH-II.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
pi-Conjugated polymers are the principal components of emerging military technologies such as fluorescent sensors for chemical agents, solar cells for battery-free machine operation in the field, and the active matrix of artificial muscles. Despite their many advantages the widespread application of these polymers has not materialized in part due to the limited polymer architectures available. One goal of my research program is to maximize the impact of organic materials by developing improved polymerization methods and expanding the spectrum of available

15. SUBJECT TERMS
polymers, microstructure, reactivity ratios

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Anne McNeil
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					734-615-5204

Report Title

Final Progress Report for New Microstructures for Old Monomers: Syntheses of Gradient pi-Conjugated Copolymers.

ABSTRACT

pi-Conjugated polymers are the principal components of emerging military technologies such as fluorescent sensors for chemical agents, solar cells for battery-free machine operation in the field, and the active matrix of artificial muscles. Despite their many advantages the widespread application of these polymers has not materialized in part due to the limited polymer architectures available. One goal of my research program is to maximize the impact of organic materials by developing improved polymerization methods and expanding the spectrum of available polymers. Current efforts are aimed at exploring the mechanisms of metal-catalyzed chain-growth polymerizations of arenes. The specific goal of this proposal is to utilize these methods to synthesize an entirely new class of organic materials – pi-conjugated gradient copolymers. Gradient copolymers exhibit a continuous change in composition and as a result have distinct thermodynamic and dynamic properties from both block and random copolymers. We predict that these novel pi-conjugated gradient copolymers may solve a long-standing problem with inconsistencies in polymer blend morphology by serving as blend compatibilizers in organic solar cells. We anticipate that the gradient copolymers will also exhibit unique optoelectronic properties. Such breakthroughs could reinvigorate the field of pi-conjugated polymers and lead to superior materials for military technologies.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

None.

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

None.

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Locke, J.R.; McNeil, A.J. Utilizing Controlled Synthesis of Conjugated Polymers to Generate New Materials, 41st National Organic Chemistry Symposium, 2009.

McNeil, A. J. Controlled Syntheses of pi-Conjugated Polymers: Mechanism and New Microstructures, Gordon Research Conference on Polymers, 2009.

McNeil, A. J. Controlled Syntheses of pi-Conjugated Polymers: Mechanism and New Microstructures, Central Regional ACS Meeting, Cope Scholar Symposium, 2009.

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

None.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

None.

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

(to be submitted in approximately 3 weeks)

Locke, J. R.; McNeil, A. J. Syntheses of pi-Conjugated Gradient Copolymers: Poly(3-hexylthiophene–grad–3-(hexyloxymethyl)thiophene).

Number of Manuscripts: 1.00

Patents Submitted

None.

Patents Awarded

None.

Graduate Students

NAME	PERCENT_SUPPORTED
Jonas Locke	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Anne McNeil	0.08	No
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

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Xiaodi (Angela) Gao	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Statement of the Problem.

Organic π-conjugated polymers are active components in emerging military technologies such as compact fluorescent sensors that warn soldiers about chemical or biological threats,[1] lightweight solar-to-electrical energy converters for operation in the field,[2] and the matrix of artificial muscles.[3] These materials have many advantages over their inorganic counterparts, including inexpensive feedstocks and the ability to be placed on flexible, large area substrates using solution-based processing and deposition methods. Though promising, the widespread application of these polymers has not materialized in part due to the limited architectures available; homopolymers are the most synthetically accessible yet they often lack one or more of the properties necessary for a functional device (e.g., efficient absorption, exciton dissociation, and charge conduction for solar cells). As a result, blends of homopolymers are typically used for these devices;[4] however, the morphology of these blends is not controlled and can depend on a number of variables, including monomer identity, polymer molecular weight, vapor pressure of deposition solvent, and annealing temperature. Though the influence of blend morphology on the efficiency of solar cells has been well documented[5] and is an active area of study,[6] a method to control and stabilize the film morphology is critically needed. Gradient copolymers, which have a continuous change in composition from one chain end to the other, have exhibited unique properties from both random and block copolymers,[7] including phase-compatibilizing abilities in homopolymer blends.[8] Prior to our work in this area (see below), there were no known examples of π-conjugated gradient copolymers because until recently there were few controlled chain-growth polymerization methods for these materials. ***In order to identify the unique properties of π-conjugated gradient copolymers, we need to synthesize these copolymers and elucidate their structure-property relationships.***

STIR Proposal Objectives

Objective 1 (Months 1-3)

Measure reactivity ratios for two pairs of monomers with the Ni- and Pd-catalysts.

(If the monomers examined in *Objective 1* have reactivity ratios suitable for copolymerization, then we will proceed to *Objective 2a*; otherwise we will pursue *Objective 2b*.)

Objective 2 (Months 4-9)

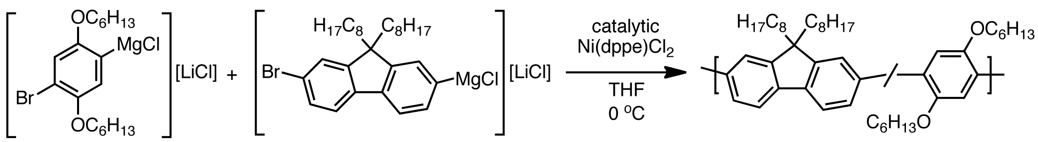
(a) Synthesize gradient π-conjugated copolymers, determine gradient composition and measure their optoelectronic properties using a combination of spectroscopic methods.

(b) Screen monomers with opposing electron densities to determine reactivity ratios.

Summary of the most important results.

Preliminary work in my group has focused on synthesizing gradient copolymers of 2,5-bis(hexyloxy)benzene and 9,9-dioctylfluorene using both batch and semi-batch methods as well as examining their unique optical and electronic properties. Our results provided (1) several novel π-conjugated gradient copolymers, (2) the first reactivity ratios measured for Ni-catalyzed copolymerization of conjugated monomers, and (3) spectroscopic evidence for efficient energy transfer in the copolymers in solution and thin films.[9] Though successful, we ran into several challenges, including a surprisingly large difference in reactivity ratios, which led to copolymers with large blocks at the termini and a short, intervening gradient region (tapered block copolymers).

Copolymer Syntheses. Although monomers **1** and **2** were reported to undergo chain-growth homopolymerizations, we needed to empirically optimize the conditions to obtain a chain-growth *co*polymerization: (1) Copious amounts of Ni black and $Ni(dppe)_2$ were observed when the copolymerizations were performed at rt. These decomposition products may be due to competitive ligand exchange and disproportionation during initiation. These processes remove unknown amounts of Ni from the polymerization and lead to uncontrolled conditions.



(1)

1 $r_1 = 0.33 \pm 0.04$

2 $r_2 = 11 \pm 1$

gradient copolymer

Performing the copolymerizations at 0 °C avoided these decomposition pathways. (2) A linear increase in M_n as a function of conversion was observed when $Ni(dppe)Cl_2$ was used as the initiator, suggesting a chain-growth mechanism. Although the polydispersity index (PDI) of the copolymer was high for a chain-growth process (~1.7), we attributed this result to a relatively slow and inefficient initiation. Surprisingly, other commercial Ni initiators reported to give chain-growth homopolymerizations, such as $Ni(dppp)Cl_2$, $Ni(dppf)Cl_2$, and $Ni(PPh_3)_2Cl_2$, did not exhibit chain-growth behavior in these copolymerizations. Ongoing work in my group is focused on developing new initiators with improved stability and initiation efficiencies.

A series of *batch* polymerizations were then carried out wherein the initial molar ratio of **1:2** was varied (3:1, 1:1, and 1:3), forming gradient copolymers with different final compositions. At the beginning of each batch copolymerization, the cumulative mole fraction of **2** incorporated into the polymer chain was higher than the initial molar ratio present in the feed, suggesting a significantly faster rate of incorporation for monomer **2**. Overall, the large difference in reactivity limits the types of gradient copolymers that can be synthesized via batch copolymerizations. Therefore, copolymers with a more gradual rate of compositional change were synthesized using the *semi-batch* method, wherein the more reactive monomer (**2**) is added to the reaction gradually over time. These studies proved challenging because chain-growth behavior was found to depend on the total monomer concentration. A linear increase in M_n was observed until the [monomer] reached approximately 0.02 M. This result is consistent with a change to a conventional step-growth mechanism at high dilution. To avoid this complication, the semi-batch syntheses were performed at higher concentrations and quenched before the total [monomer] reached 0.02 M. Overall, the variety of gradient copolymers synthesized was limited due to the narrow range of [monomer] that gave chain-growth behavior. These results suggest that future studies should focus on different monomers and possibly different catalysts.

Reactivity Ratios. To quantify the reactivity differences, the reactivity ratios were determined through a series of experiments wherein the initial concentrations of **1** and **2** were varied. The rates of monomer consumption were followed for the first 30% conversion by IR spectroscopy. This data was fit with a least-squares regression to the integrated copolymerization equation (eq 2), where $(f_1)_0$ and f_1 are the mole fractions of monomer **1** in the feed initially and at time t, respectively. In total, over 40 experiments at 8 different concentrations were simultaneously fit to determine the reactivity ratios, which reflect the rate preference for a propagating species to add its own type of monomer over the other. Consistent with our qualitative observations, monomer **1** gave a reactivity ratio (r_1) of 0.33 ± 0.04 while monomer **2**

gave a reactivity ratio (r_2) of 11 ± 1. These values indicate that the growing polymer chain prefers to add **2** over **1** regardless of the identity of the previously added monomer unit. Since **1** has an *ortho*-substituent, we hypothesize that steric interactions of **1** with the catalyst may be leading to a diminished rate relative to **2**. The electronic differences between the two monomers may also be a contributing factor. Given this limited data set, we plan to further probe this issue using the monomers described in Aim 1.

$$1 - \frac{[M]}{[M]_0} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha}\left[\frac{1 - f_1}{1 - (f_1)_0}\right]^{\beta}\left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma} \quad (2)$$

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \qquad \alpha = \frac{r_2}{(1 - r_2)} \qquad \gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)} \qquad \beta = \frac{r_1}{(1 - r_1)} \qquad \delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

Copolymer Characterization. UV-vis and fluorescence spectroscopy were used to characterize the optical properties of these novel gradient copolymers (Figure 1). The gradient copolymers absorb at wavelengths corresponding to each of the homopolymers with different maxima depending on the final composition. Given that these copolymers have large blocks of each monomer at the termini, it was surprising that all of their emission spectra show a maximum around 430 nm, which coincides with the emission from polyfluorene homopolymer; this result suggests that there is highly efficient intrachain energy transfer in solution. Thin film spectroscopic studies revealed similar trends. Further characterization studies were not pursued due to the limited microstructures available from these monomers and Ni(dppe)Cl_2.

In summary, these studies have led us to conclude: (1) π-Conjugated gradient copolymers can be synthesized using Ni-catalyzed chain-growth methods; however, with existing catalysts, the reaction conditions must be optimized for each pair of monomers. (2) Steric effects between the catalyst and monomer may play a significant role in reactivity ratios. (3) These gradient copolymers exhibit efficient energy transfer in solution and thin films. More gradient copolymers need to be synthesized to elucidate the role of comonomer identity, copolymer sequence, composition, and molecular weight on the copolymer properties.

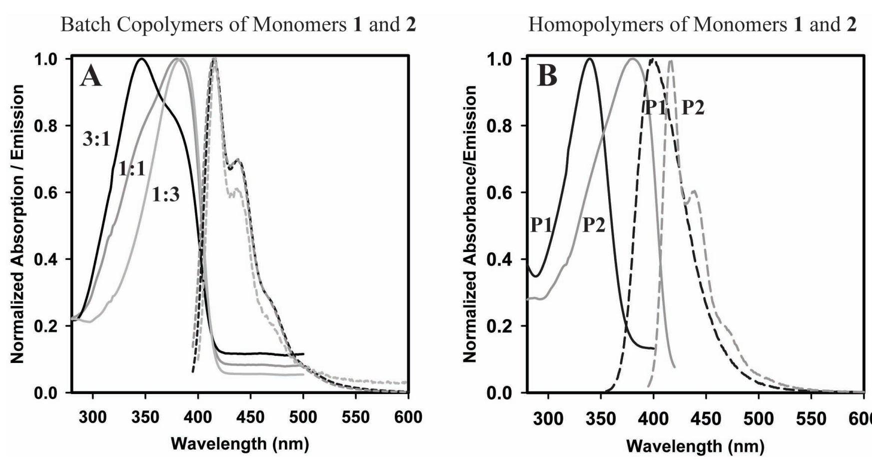


Figure 1. Absorption (solid lines) and emission (dashed lines) spectra for (A) batch copolymers at varying **1:2** ratios and (B) homopolymers in solution.

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